

This Page Is Inserted by IFW Operations  
and is not a part of the Official Record

## **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

**IMAGES ARE BEST AVAILABLE COPY.**

As rescanning documents *will not* correct images,  
please do not report the images to the  
Image Problem Mailbox.

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>C08L 29/04, 67/04 // (C08L 29/04, 67:04)</b> <b>(C08L 67/04, 29:04)</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 98/29506</b> <b>(43) International Publication Date:</b> 9 July 1998 (09.07.98)
<b>(21) International Application Number:</b> PCT/US97/22794 <b>(22) International Filing Date:</b> 12 December 1997 (12.12.97) <b>(30) Priority Data:</b> 08/774,730 31 December 1996 (31.12.96) US <b>(71) Applicant:</b> KIMBERLY-CLARK WORLDWIDE, INC. [US/US]; 401 North Lake Street, Neenah, WI 54956 (US). <b>(72) Inventors:</b> WANG, James, Hongxue; 1325 E. Overland Road, Appleton, WI 54915 (US). SCHERTZ, David, Michael; Apartment 301, E. Water Street, Appleton, WI 54915 (US). SOERENS, Dave, Allen; 736 Kensington Road, Neenah, WI 54956 (US). <b>(74) Agents:</b> WARREN, William, L.; Jones & Askew, 37th floor, 191 Peachtree Street, N.E., Atlanta, GA 30303 (US) et al.		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> WATER-RESPONSIVE POLYMER COMPOSITIONS AND METHOD OF MAKING THE SAME		
<b>(57) Abstract</b>  Selectively water-responsive polymer blend compositions constructed of combinations of polymers including polylactic acid and polyvinyl alcohol are provided. A method of making a selectively water-sensitive homogenous polymer blend composition, comprising combining polylactide and polyvinyl alcohol at a temperature above the melting point of the polymer having the higher melting point, and below the decomposition point of the polymer having the lower decomposition point, to form a homogeneous polymer blend composition is also provided. The water-responsive properties of the polymer blend compositions include water-dispersible, water-disintegratable, water-weakenable, and water-stable.		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon	KR	Republic of Korea	PL	Poland		
CN	China	KZ	Kazakhstan	PT	Portugal		
CU	Cuba	LC	Saint Lucia	RO	Romania		
CZ	Czech Republic	LI	Liechtenstein	RU	Russian Federation		
DE	Germany	LK	Sri Lanka	SD	Sudan		
DK	Denmark	LR	Liberia	SE	Sweden		
EE	Estonia			SG	Singapore		

5

10

## **WATER-RESPONSIVE POLYMER COMPOSITIONS AND METHOD OF MAKING THE SAME**

### **FIELD OF THE INVENTION**

15

20

The present invention relates to selectively water-responsive polymer blend compositions, and methods of use and manufacture thereof. The polymer blend compositions have a wide range of water-responsiveness ranging from water-dispersible, to water-disintegratable, to water-weakenable and water-stable. These polymer blend compositions can also be water temperature sensitive, and are particularly suited for use in the manufacture of disposable products.

### **BACKGROUND OF THE INVENTION**

25

30

35

Even though the amount of plastics used in a variety of consumer goods, packaging and medical articles has not significantly increased over the past twenty years, the common perception is that more and more non-degradable plastics are filling up our landfills. Plastics offer many advantages over the more traditional wood, glass, paper, and metal articles including improved performance, comparable or decreased cost of manufacture and decreased transportation costs. Disposal of all waste materials, including food waste, packaging materials, medical waste into a typical landfill provides a relatively stable environment in which none of these materials is seen to decompose at an appreciable rate. Alternative waste disposal options are increasingly discussed and utilized to divert some fractions of waste from entombment. Examples of these

alternatives include municipal solid waste composting, anaerobic digestion, enzymatic digestion, and waste water sewage treatment.

Much controversy is associated with the disposal of medical waste. Both government agencies and members of the public sector have been increasingly directing in-depth scrutiny toward this subject. Admittedly, concerns over the fate of materials contaminated with infectious substances are valid and proper measures to insure the safety of health care workers and the general public should be taken.

Currently, medical waste can be categorized into reusable and disposable. Categorization as to whether certain waste is reusable or disposable is customarily determined according to the material from which the article was constructed and the purpose for which the article was used.

After use, reusable medical articles are cleansed and sterilized under stringent conditions to ensure disinfection. In comparison, disposable medical articles are usually only used once, and even then, disposing procedures are not straightforward, rather they often involve several steps to safeguard against potential hazards. Typically, after use, disposable medical articles must be disinfected or sterilized, adding a significant cost prior to disposal into a specially designated landfill or waste incinerator. As a result, the disposal cost for the contaminated single use articles is quite high.

Despite the high cost of disposal, single use medical articles are desirable because of the assurance of clean, and uncontaminated equipment. Many times in the medical context, sterilization procedures conducted improperly can result in detrimental effects such as the transmission of infectious agents from one patient to another. Improper sterilization can also be disastrous in a laboratory setting, where, for example, contaminated equipment can ruin experiments resulting in tremendous costs of time and money.

Currently, disposable medical fabrics are generally composed of thermoplastic fibers such as polyethylene, polypropylene, polyesters, polyamides and acrylics. They are typically 10-100 grams per square yard in weight and can be woven, knitted or otherwise formed by methods well known to

those in the textile arts while the non-wovens can be thermobonded, hydroentangled, wet laid or needle punched and films can be formed by blow or cast extrusion or by solution casting.

5           The use of polymers for various disposable articles is widespread and well known in the art. In fact the heaviest use of polymers in the form of film and fibers occurs in the packaging and disposable article industries. Films and fibers employed in the packaging industry include those used in food and non-food  
10 packaging, merchandise bags and trash bags. In the disposable article industry, the general uses of polymers occurs in the construction of diapers, personal hygiene articles, surgical drapes and hospital gowns, instrument pads, bandages, and protective covers for various objects.

15           In light of depleting landfill space and inadequate disposal sites, there is a need for polymers which are water-responsive. Currently, although polymers such as polyethylene, polypropylene, polyethylene terephthalate, nylon, polystyrene, polyvinyl chloride and polyvinylidene chloride are popular for  
20 their superior extrusion and film and fiber making properties, these polymers are not water-responsive. Furthermore, these polymers are generally non-compostable, which is undesirable from an environmental perspective.

          Polymers and polymer blends, have been developed  
25 which are generally considered to be water-responsive. These are polymers which purportedly have adequate properties to permit them to breakdown when exposed to conditions which lead to composting. Examples of such arguably water-responsive polymers include those made from polyethylene oxide, starch  
30 biopolymers and polyvinyl alcohol.

          Although polymers extruded from these materials have been employed in film and fiber containing articles, many problems have been encountered with their use. Often the polymers are not completely water-responsive or compostable.  
35 Furthermore, some water-responsive polymers may also be unduly sensitive to water, either limiting the use of the polymer or requiring some type of surface treatment to the polymer, often rendering the polymer non water-responsive. Other polymers are

undesirable because they have inadequate heat resistance for wide spread use.

Personal care products such as diapers, sanitary napkins, adult incontinence garments, and the like are generally constructed from a number of different components and materials. Such articles usually have some portion, usually the backing layer constructed of a liquid repellent or non water-responsive polymer material. The non water-responsive material commonly used includes plastic materials such as polyethylene film or copolymers of ethylene and other polar and nonpolar monomers. The purpose of the non water-responsive layer is to minimize or prevent absorbed liquid that may, during use, exude from the absorbent and soil the user or adjacent clothing. The non water-responsive layer also has the advantage of allowing greater utilization of the absorbent capacity of the product.

Although such products are relatively inexpensive, sanitary and easy to use, disposal of a soiled product is not without its problems. Typically, the soiled products are disposed in a solid waste receptacle. This adds to solid waste disposal costs and presents health risks to persons who may come in contact with the soiled product. An ideal disposal alternative would be to use municipal sewage treatment and private residential septic systems by flushing the soiled product in a toilet. Products suited for disposal in sewage systems are termed "flushable". While flushing such articles would be convenient, the non water-responsive material currently used in personal care products, normally does not disintegrate in water. This tends to plug toilets and sewer pipes, frequently necessitating a visit from a plumber. At the municipal sewage treatment plant, the non water-responsive material may disrupt operations by plugging screens and causing sewage disposal problems. It therefore becomes necessary, although undesirable, to separate the barrier film material from the absorbent article prior to flushing.

In addition to the article itself, typically the packaging in which the disposable article is distributed is also made from a non water-responsive, specifically water-resistant, material. Water-resistivity is necessary to prevent the degradation of the packaging from environmental conditions and

to protect the disposable articles therein. Although this packaging may be safely stored with other refuse for commercial disposal, and especially in the case of individual packaging of the products, it is often more convenient to dispose of the packaging in the toilet with the discarded disposable article. However, where such packaging is composed of a water-resistant material, the  
5                   aforementioned problems persist.

          The use of lactic acid and lactide to manufacture a water-responsive polymer is well known in the medical industry. Such polymers have been used in the past for making sutures, clamps, bone plates and biologically active controlled release devices. Processes developed for the manufacture of such polymers to be utilized in the medical industry have incorporated techniques which respond to the need for high purity and  
10                   biocompatibility in the final product. These processes, however, are typically designed to produce small volumes of high dollar-value products, with less emphasis on manufacturing cost and yield.

          It is generally known that lactide polymers or poly(lactides) are unstable, however, the consequence of this instability has several aspects. One aspect is biodegradation or hydrolysis which occurs when lactide polymers, or articles manufactured from lactide polymers, are discarded or composted after completing their useful life. Another aspect of such  
20                   instability is the degradation of lactide polymers during processing at elevated temperatures as, for example, during melt-processing by end-user purchasers of polymer resins.

          In the medical area there is a predominant need for polymers which are highly stable and therefore desirable for use in medical devices. Such a demand has historically been prevalent  
30                   in the high value, low volume medical specialty market, but is now also equally prevalent in the low value, high volume medical market.

          As described in U.S. Patent No. 5,472,518, compositions comprised of multilayer polymer films are known  
35                   in the art. The utility of such structures lies in the manipulation of physical properties in order to increase the stability or lifetime during use of such structure. For example U.S. Patent No.



4,826,493 describes the use of a thin layer of hydroxybutyrate polymer as a component of a multilayer structure as a barrier film for diaper components and ostomy bags.

Another example of use of multilayer films is found in U.S. Patent No. 4,620,999 which describes the use of a water-soluble film coated with, or laminated to, a water-insoluble film as a disposable bag. The patent describes a package for body waste which is stable to human waste during use, but which can be made to degrade in the toilet, at a rate suitable for entry into a sewage system without blockage, by adding a caustic substance to achieve a pH level of at least 12. Such structures are usually consist of a polyvinyl alcohol film layer coated with polyhydroxybutyrate.

A similar excretion-treating bag allowing discarding in flush toilet or sludge vessel is disclosed in JP 6142127. It is composed of an inner layer of water-resistant resin such as polylactide and an outer layer of water-soluble polyvinyl alcohol. As disclosed in this patent, there are many examples of multilayer films that are utilized in disposable objects. Most of these examples consist of films or fibers which are comprised of external layers of an environmentally degradable polymer and an internal layer of water-responsive polymer. Typically, the external layers are comprised of polyolefin, polycaprolactone, or ethylene vinyl acetate and the internal layer is comprised of polyvinyl alcohol. These examples, however, are all limited to compositions consisting of multilayers of different polymers, and do not encompass actual blends of different polymers.

Another family of patents, including EP 241178, JP 62223112, and U.S. Patent No. 4,933,182, describes a controlled release composition for treating periodontal disease. The compositions are comprised of a therapeutically effective agent in a two-phase carrier consisting of a continuous phase and a discontinuous phase. The continuous phase consists of a water-soluble polymer and the discontinuous phase consists of a polymer of limited water solubility. Although the compositions of these inventions include the use of more than one polymer, the polymers are utilized in layers and not as intermingled or blended components.

The use of polymer blends for use in water-responsive articles is also disclosed in U.S. Patent No. 5,508,101, U.S. Patent No. 5,567,510, and U.S. Patent No. 5,472,518. This group of patents discloses a series of water-responsive compositions comprising a hydrolytically degradable polymer and a water-soluble polymer. The compositions of this group, however, consist of articles constructed from polymers which are first formed into fibers or films and then combined. As such, the compositions are actually mini-layers of the individual polymer films or fibers. Therefore, although the fibers and films of the polymers of such compositions are considered to be in very close proximity with one another, they are not actual polymer blends made by melting the polymers into a homogenous molten mixture. The dispersion of one polymer within another in these compositions, is not viewed as homogenous since the individual polymers are essentially distinct and separate fibers or films.

Polymer blend compositions consisting of fibers and films that are optimally combined are desirable because they are highly stable. Optimal combination of polymers means wherein polymers are connected as closely as possible without the requirement of polymerization. Although blended polymer compositions are known, improved polymer blends wherein the fibers and films are more intimately connected are desirable since the resulting composition is then more stable, pliable and versatile.

In addition to the need for polymer compositions that are highly stable, and therefore suitable for regular use in most disposable articles, there is a simultaneous need for such polymer compositions to be water-responsive. What is needed therefore, is a material that may be utilized for the manufacture of disposable articles and which is water-responsive. Such material should be versatile and inexpensive to produce. The material should be stable enough for intended use but subject to degradation under predetermined conditions.

## SUMMARY OF THE INVENTION

The present invention provides selectively water-responsive compositions made from polymers such as polylactide

and polyvinyl alcohol, and products constructed therefrom. Desirably, the products are designed for a single use, and then for disposal in cold water such as by flushing in a toilet.

5 Products used according to the present invention comprise water-responsive polymer compositions. The term "water-responsive", as used herein, means that the compositions are either water-dispersible, water-disintegratable, water-weakenable or water-stable. The degree of water-responsiveness may vary depending upon the composition of the polymers, chemical or manufacturing modifications thereto, and the  
10 temperature of the water, for example.

Products of the present invention are constructed of combinations of polymers including polylactic acid (PLA), polyvinyl alcohol (PVOH), and polyhydroxybutyrate-co-valerate and polyethylene succinate (BINOLLI®), for example. Products  
15 of the present invention are constructed of compositions comprising 'hydrolytically degradable' polymers and 'water-soluble' polymers. The term "hydrolytically degradable", as used herein, means degradation by hydrolysis and nonlimiting types of hydrolytically degradable polymers including polylactic acid (hereinafter "PLA"), polyester amides (hereinafter "PEA"), polyglycolic acid (hereinafter "PGA"), and polyhydroxybutyrate-co-valerate (hereinafter "PHBV"), and the like; and combinations thereof as copolymers, blends, mixtures and the like. The term  
20 "water-soluble", as used herein, means that the polymer will completely dissolve upon extended contact with water. Nonlimiting types of water-soluble polymers include polyvinyl alcohol (hereinafter "PVOH"), polyaspartic acid, polyacrylic acid, polymethacrylic acid, polyacrylamide, polyvinyl pyrrolidone, polyalkylene oxides, complex carbohydrates and combinations thereof as copolymers, blends, mixtures, and the like.  
25 30

The present invention discloses selectively water-responsive polymer blend compositions of films and fibers having a wide range of water-responsiveness: water-dispersible, water-disintegratable, water-weakenable and water-stable. The  
35 present invention also discloses methods of manufacture for water-responsive polymer blend compositions of films and fibers to suit for different application needs. The composition ranges

responsible for each type of water-responsiveness are also disclosed. The compositions of the present invention are useful as components in flushable personal care products, such as the outer cover film for diapers, the laminating film for clothlike outer cover, baffle film for feminine pads and pantliners, etc. In addition to flushability, the compositions of the present invention have the advantage of being biodegradable so that the materials will degrade in anaerobic digesters and aeration tanks in waste water treatment plants and will not increase the volume of sludge.

These and other features and advantages of the present invention will become apparent after a review of the following detailed description of the disclosed embodiments.

#### DETAILED DESCRIPTION

The present invention provides selectively water-responsive polymer blend compositions of film or fiber-based products configured into such fabrics, garments and articles as drapes, towels, covers, overwraps, gowns, head coverings, face masks, shoe coverings, CSR wraps, sponges, dressings, tapes, underpads, diapers, liners, wash cloths, sheets, pillow covers, napkins, cloth-like outercovers, feminine tampons, pads and pantliners, and baffle films therefor, and any woven, non-woven, or otherwise formed materials. Such products can be employed in the medical industry both in hospitals, outpatient facilities and in home environments.

Many of these products generally come into contact with human bodily fluids and their disposal and disinfection has become a matter of major concern in light of the lack of biodegradability of prior products and the potential spread of human fluid-born diseases such as hepatitis B and AIDS.

To overcome these difficulties, the present invention provides that products employed in the manufacture of such items be composed of polymer blend compositions, of films or fibers, which are water-responsive, either alone or with the addition of surfactants, salts and bleaches. The invention provides that the relative amounts of the polymers and modifiers in the inventive compositions may be adjusted to increase or decrease the solubility of the products made therefrom in water.

The present invention includes compositions and methods for the production of selectively water-responsive polymer blends. These water-responsive polymer blends are constructed from water-soluble and hydrolytically degradable polymers including polylactic acid (PLA), polyvinyl alcohol (PVOH), and polyhydroxybutyrate-co-valerate (PHBV). PLA, in the form of lactide copolymers with other cyclic esters, imparts properties such as softness and pliability, and therefore can be used for certain embodiments of the present invention. Cold-water soluble polyvinyl alcohol (PVOH) of partially hydrolyzed polyvinyl acetate is desired for the compositions of the present invention and typically the hydrolysis level is between approximately 70% and 85%. The term "hydrolysis level" as used herein, is defined as the percentage of vinyl acetate units in polyvinyl acetate which are hydrolyzed into vinyl alcohol units in the polyvinyl alcohol. The PHBV resins for the present invention can be made by either the fermentation process of carbohydrate and an organic acid by a micro-organism, e.g. *Alcaligenes eutrophus*, or by the use of transgenic plants. ("Biodegradable Plastics from Plants", CHEMTECH, September 1996, ppgs. 38-44).

Depending upon the purpose and use of an article, compositions comprising different components of variable water-sensitivity may be desired. Controlling water-responsiveness is necessary for different components in certain products due to the location of use in relation to body waste. For example, a diaper backsheet may be desirably water-weakenable, whereas the absorbent filler may be desirably water-dispersible. The ability to determine and predict the water-sensitivity of specific polymer blend compositions is therefore an important aspect of the present invention.

The selectively water-responsive polymers of the present invention are particularly desirable and unique because of their water-responsive qualities. Generally, depending on individual compositions and blends of polymers, as well as the method of manufacture of the blends, the water-responsiveness of the resulting material may be manipulated and determined. The degree of water-responsiveness that may be determined according

to the compositions and methods of the present invention include water-dispersible, water-disintegratable, water-weakenable and water-stable.

5 Generally, manufacturers of polymers utilizing standard processes convert raw material monomers into polymer beads, resins or other pelletized or powdered products, which are commercially available from companies such as Aldrich (Milwaukee, Wisconsin), Dow Chemical (Midland, Michigan), DuPont Company (Wilmington, DE), Exxon (Baytown, TX),  
10 Nippon Goshei (Japan) and Union Carbide Corporation (Danbury, CT). The polymer in this form may then be used in processes such as extruding, blow-molding, casting films, blowing films, thermoforming, injection-molding or fiber-spinning at elevated temperatures, for example, to form useful articles. The above  
15 processes are collectively referred to as melt-processing. Polymers produced by processes which are to be provided commercially as beads, resins powders or other non-finished solid forms are generally referred to collectively as polymer resins.

PLA resins produced by different synthetic methods  
20 such as ring-opening polymerization of lactide or direct condensation polymerization from lactic acid are particularly useful for the compositions according to the present invention. PLA ( $M_n = 60,000$ ,  $T_g$  (glass transition temperature) =  $60^\circ\text{C}$ ,  $M_w = 144,000$ , 96.8% L-Isomer), purchased from Aldrich Chemical  
25 Co., Milwaukee, WI, was used in the examples. Cold water soluble PVOH (Ecomaty AX 10000), purchased from Nippon Gohsei, Japan, is also an exemplary type resin that was used in the examples.

The hydrolytically degradable and water-soluble  
30 polymer blend compositions according to the present invention are produced by a melt mixing process. It is desired according to the present invention to blend or mix the two components in an extruder, such as a single-screw or twin-screw extruder under appropriate temperature and shear/pressure conditions to ensure  
35 mixing. The blending process can also be performed in a batchwise mixing device, such as a melt mixer or a kneader. PLA or PVOH can be fed into the extruder/mixer either simultaneously or in sequence.

The present invention discloses selectively water-responsive homogenous polymer blend compositions comprising hydrolytically degradable and water-soluble polymer blend such as polylactide and polyvinyl alcohol. The term "homogeneous polymer blend composition", as used herein, means that the polymer blend forms a cohesive, continuous structure of polylactide and polyvinyl alcohol. A homogenous polymer blend composition can be achieved by the mixing of polylactide and polyvinyl alcohol at temperatures above the melting point of the polymer having the highest melting point, and below the decomposition point of the polymer having the lowest decomposition point, in order to form a homogeneous molten mixture of the polymers (prior to cooling to solid form, e.g. films or fibers). For homogenous polymer blend compositions of polylactide and polyvinyl alcohol, the polymer having the higher melting point is polyvinyl alcohol and the polymer having the lower decomposition point is also polyvinyl alcohol. The melting point for polyvinyl alcohol is generally approximately between 180-190°C, and more specifically around 183°C. The decomposition point of polyvinyl alcohol is above approximately 200°C. The resulting composition resembles islands of polylactide in a sea of polyvinyl alcohol, for example, and at a microscopic level has the appearance of approximately uniform distribution of polylactide among polyvinyl alcohol. The homogeneous polymer blend composition of the present invention therefore has a very fine dispersion of polylactide within polyvinyl alcohol.

Based upon the uniformity of dispersion, the "polymer blend" of the present invention is distinguishable from "blended polymers." The compositions of the present invention comprise polymers that are blended above the melting point of the polymer having the highest melting point (polyvinyl alcohol), and below the decomposition points of the polymer having the lowest decomposition point (polyvinyl alcohol). The homogeneous polymer blend composition, therefore, is formed prior to the polymers being formed into films or fibers, resulting in compositions of polymers which are highly, and intimately interconnected, having a selectively uniform dispersion. Such

compositions are distinguishable from those comprising blended polymers that consist of polymers which are blended after they have been formed into fibers or films, resulting in compositions which do not have approximate uniform dispersion and often appearing as individual polymers layered or mixed together. Summarily, when individual polymers are mixed at temperatures above the melting point of the polymer having the highest melting point, and below the decomposition point of the polymer having the lowest decomposition point, an approximately uniform distribution and dispersion of polymers results. In contrast, when individual polymers are mixed according to standard practices, a blended polymer composition results wherein the polymers are not as integrally associated.

The water-sensitivity of the polymer compositions may be controlled according to the degree of the homogeneity of the polymer blends. Mixing, sheering, extrusion and other blending techniques, as well as the relative proportions of the polymer resins used, may be manipulated to determine the microstructure of polymer compositions. The 'microstructure' of the polymer blends refers specifically to the size and distribution of polylactide islands within the polyvinyl alcohol sea, for example. The size of the islands may vary from approximately 0.1 to 5.0 $\mu$ m. Generally, as the size of the islands increases, and/or as the distance between them decreases, the composition gains greater mechanical strength and loses pliability. For example, for water-dispersible compositions, the islands are typically small (approximately 0.2-1.0 $\mu$ m), and are distributed so that they are far apart from each other. For water-disintegratable compositions, the islands are closer together, with a few islands that may even be connected to one another. For water-weakenable compositions, the islands can be in very close proximity and a majority of them appear as large clumps.

One embodiment of the present invention is a homogeneous polymer blend composition comprising approximately 1-35% polylactide and approximately 65-99% polyvinyl alcohol, wherein such composition is water-dispersible. The term "water-dispersible", as used herein, means that the composition will dissolve or break into pieces smaller than a 20



mesh after being tested with water at room temperature (18-22°C) for 2 minutes. "Testing with water", as used herein, means preparing a sample of the composition then immersing it into a scintillation vial filled with water for 5 minutes, followed by shaking the vial for approximately 30 seconds in a mechanical shaking device, and then emptying the contents of the vial through a standard 20 mesh screen.

Another embodiment of the present invention is a homogeneous polymer blend composition comprising approximately 35-45% polylactide and approximately 65-55% polyvinyl alcohol, wherein such composition is water-disintegratable. The term "water-disintegratable" as used herein, means that the composition will break into multiple pieces after 2 minutes and that some of the composition pieces will be caught by a 20 mesh screen.

One other embodiment of the present invention is a composition comprising approximately 45-55% polylactide and approximately 55-45% polyvinyl alcohol, wherein such composition is water-weakenable. The term "water-weakenable", as used herein, means that the composition remains in one piece but weakens and loses rigidity after 5 minutes and becomes drapeable, i.e., it bends without an external force applied to the composition when it is held by one corner at a horizontal position.

Yet another embodiment of the present invention is a composition comprising approximately 55-99% polylactide and approximately 45-1% polyvinyl alcohol, wherein such composition is water-stable. The term "water-stable", as used herein, means that the composition does not become drapeable and remains in one piece after testing with water.

The compositions of the present invention may be formed into polymer fibers or into polymer films.

A method of making a selectively water-sensitive homogenous polymer blend composition, comprises combining hydrolytically degradable polymers, such as polylactide, and water-soluble polymers, such as polyvinyl alcohol, at a temperature above the melting point of the polymer having the highest melting point, and below the decomposition point of the polymer having the lowest decomposition point, to form a

homogeneous polymer blend composition.

For making a composition that is selectively water-dispersible, approximately 1-35% polylactide and approximately 65-99% polyvinyl alcohol are combined. For making a composition that is selectively water-disintegratable, approximately 35-45% polylactide and approximately 65-55% polyvinyl alcohol are combined. For making a composition that is selectively water-weakenable, approximately 45-55% polylactide and approximately 55-45% polyvinyl alcohol are combined. For making a composition that is selectively water-stable, approximately 55-99% polylactide and approximately 45-1% polyvinyl alcohol are combined.

Processing characteristics of the polymer blends for films can be enhanced by the optional incorporation of lubricants or slip agents into the blends. Such lubricants are well known in the art and include TWEEN 20, TURGITOL NP 13 available from Union Carbide Corporation (Danbury, CT) and various fatty acids such as KENAMIDE E available from Witco Chemical (USA). In addition, the blends may contain other components to enhance the properties of the resulting material. For example, polyethylene glycol can be added to lower the melt viscosity of the melted blend to a range suitable for other processes such as meltblown or meltsprayed nonwoven materials. Suitable polyethylene glycols are available from Union Carbide under the tradename CARBOWAX®.

Polymer blending is an important aspect of the manufacture of the present invention compositions. Depending upon parameters such as the selection of blending techniques, temperature profiles, and pressure applications, the final water-responsive qualities of the compositions may be affected.

The polymer blending process for water-responsive compositions containing hydrolytically degradable polymers, such as PLA, and water-soluble polymers, such as PVOH, desirably involves the use of an extruder. Desirably, the two polymer components are blended or mixed in an extruder such as a single-screw or a twin-screw extruder under appropriate temperature and shear/pressure conditions. The blending process can also be performed in batchwise mixing devices such as a melt

mixer or a kneader. Both PVOH and PLA can be fed to an extruder either simultaneously or in sequence to minimize any adverse effects on the polymers such as degradation or discoloration.

5           The present invention is further illustrated by the following examples, which are not to be construed in any way as imposing limitations upon the scope of the claims. On the contrary, it is to be clearly understood that resort may be had to various other embodiments, modifications, and equivalents thereof, which, after reading the description herein, may suggest themselves to those skilled in the art without departing from the spirit of the present invention.

#### Example 1

15           For the following examples, a section of the prepared film was cut measuring about 1/4 of an inch by about 1/2 of an inch. The water-response test involved using a pair of tweezers to hold the section of the film, immersing it into a scintillation vial filled with 20 milliliters of water and holding it there for 5 minutes. After 5 minutes, the cap was placed on the scintillation vial and the vial was placed in a Model 75 Shaker (available from Burrell Corp., Pittsburgh, PA). The vial was shaken for 30 seconds with the shaker set a maximum speed. If the film began to disperse or disintegrate, the contents of the scintillation vial were emptied through a 20 mesh screen (20 mesh U.S.A. Standard Testing Sieve, ASTM E-11 Specification, No. 20). The vial was then rinsed with 20 milliliter of water from a squeeze bottle to remove any remaining film pieces and emptied through the sieve.

25           If the film did not disperse or disintegrate, the film was observed for any loss in rigidity.

#### Example 2

35           A blend containing 21 grams of polylactide and 49 grams of polyvinyl alcohol was prepared using a Haake Rheomix 600 twin-roller mixer (available from Haake, Paramus, New Jersey). Each zone of the Haake mixer was preheated to 180°C. The polymer melt temperature after 5 minutes was about 184°C.

The material was mixed for 5 minutes at a screw speed of 150 rpm. After 5 minutes, the melt was removed from the mixer and cooled in air. A film (approximately 5 mil thick) was prepared from the composition using a Carver hot press with two heated platens at a temperature of 190°C and a pressure of 15000psi for 1 minute.

The film was determined to be water-dispersible under the water-response test.

### Example 3

A blend containing 28 grams of polylactide and 42 grams of polyvinyl alcohol was prepared using a Haake Rheomix 600 twin-roller mixer (available from Haake, Paramus, New Jersey). Each zone of the Haake mixer was preheated to 180°C. The polymer melt temperature after 5 minutes was about 196°C. The material was mixed for 5 minutes at a screw speed of 150 rpm. After 5 minutes, the melt was removed from the mixer and cooled in air. A film (approximately 5 mil thick) was prepared from the composition using a Carver hot press with two heated platens at a temperature of 190°C and a pressure of 15000psi for 1 minute.

The film was determined to be water-disintegratable under the water-response test.

### Example 4

A blend containing 35 grams of polylactide and 35 grams of polyvinyl alcohol was prepared using a Haake Rheomix 600 twin-roller mixer (available from Haake, Paramus, New Jersey). Each zone of the Haake mixer was preheated to 180°C. The polymer melt temperature after 5 minutes was about 196°C. The material was mixed for 5 minutes at a screw speed of 150 rpm. After 5 minutes, the melt was removed from the mixer and cooled in air. A film (approximately 5 mil thick) was prepared from the composition using a Carver hot press with two heated platens at a temperature of 190°C and a pressure of 15000psi for 1 minute.

The film was determined to be water-weakenable under the water-response test.

### Example 5

A blend containing 42 grams of polylactide and 28 grams of polyvinyl alcohol was prepared using a Haake Rheomix 600 twin-roller mixer (available from Haake, Paramus, New Jersey). Each zone of the Haake mixer was preheated to 180°C. The polymer melt temperature after 5 minutes was about 189°C. The material was mixed for 5 minutes at a screw speed of 150 rpm. After 5 minutes, the melt was removed from the mixer and cooled in air. A film (approximately 5 mil thick) was prepared from the composition using a Carver hot press with two heated platens at a temperature of 190°C and a pressure of 15000psi for 1 minute.

The film was determined to be water-weakenable under the water-response test.

### Example 6

A resin mixture of 20/80 PLA/PVOH, by weight, was added to a Haake TW-100 twin-screw extruder with counter-rotating conical screws mixer (available from Haake, Paramus, New Jersey) at 10 lb/hr. The polymer melt temperature during the extrusion was about 186°C. The barrel set temperatures were 170°C, 180°C, 180°C and 168°C. The screw speed was 150 rpm. Melt strands were cooled by air on a conveyor belt and pelletized. A thin film was prepared under the same conditions as Example 2.

The film was determined to be water-dispersible under the water-response test.

### Example 7

A resin mixture of 30/70 PLA/PVOH, by weight, was added to a Haake TW-100 twin-screw extruder with counter-rotating conical screws mixer (available from Haake, Paramus, New Jersey) at 10 lb/hr. The polymer melt temperature during the extrusion was about 187°C. The barrel set temperatures were 170°C, 180°C, 180°C and 168°C. The screw speed was 150 rpm. Melt strands were cooled by air on a conveyor belt and pelletized. A thin film was prepared under the same conditions as Example

2.

The film was determined to be water-dispersible under the water-response test.

5 Those skilled in the art will now see that certain modifications can be made to the invention herein disclosed with respect to the illustrated embodiments, without departing from the spirit of the instant invention. And while the invention has been described above with respect to the preferred embodiments, it will be understood that the invention is adapted to numerous  
10 rearrangements, modifications, and alterations, all such arrangements, modifications, and alterations are intended to be within the scope of the appended claims.

## Claims

What is claimed is:

- 5                   1.    A water-sensitive homogenous polymer blend composition comprising polylactide and polyvinyl alcohol.
2.    The composition of Claim 1, wherein the composition comprises approximately 1-35% polylactide and  
10                   approximately 65-99% polyvinyl alcohol, and wherein such composition is water-dispersible.
3.    The composition of Claim 1, wherein the composition comprises approximately 35-45% polylactide and  
15                   approximately 65-55% polyvinyl alcohol, and wherein such composition is water-disintegratable.
4.    The composition of Claim 1, wherein the composition comprises approximately 45-55% polylactide and  
20                   approximately 55-45% polyvinyl alcohol, and wherein such composition is water-weakenable.
5.    The composition of Claim 1, wherein the composition comprises approximately 55-99% polylactide and  
25                   approximately 45-1% polyvinyl alcohol, and wherein such composition is water-stable.
6.    The composition of Claim 1, wherein the composition is formed into a film.
- 30                   7.    A method of making a selectively water-sensitive homogenous polymer blend composition, comprising combining polylactide and polyvinyl alcohol at a temperature above the melting point of polyvinyl alcohol, and below the  
35                   decomposition point of polyvinyl alcohol, to form a homogeneous polymer blend composition.

8. The method of Claim 7, wherein the melting point of polyvinyl alcohol is approximately between 180-190°C, and wherein the decomposition point of polyvinyl alcohol is approximately 200°C.

5

9. The method of Claim 7 wherein the wherein the melting point of polyvinyl alcohol is 183°C.

10

10. The method of Claim 7, wherein approximately 1-35% polylactide and approximately 65-99% polyvinyl alcohol are combined, and wherein such composition is selectively water-dispersible.

15

11. The method of Claim 7, wherein the composition comprises approximately 35-45% polylactide and approximately 65-55% polyvinyl alcohol, and wherein such composition is selectively water-disintegratable.

20

12. The method of Claim 7, wherein the composition comprises approximately 45-55% polylactide and approximately 55-45% polyvinyl alcohol, and wherein such composition is selectively water-weakenable.

25

13. The method of Claim 7, wherein the composition comprises approximately 55-99% polylactide and approximately 45-1% polyvinyl alcohol, and wherein such composition is selectively water-stable.

30

14. A composition comprising a water-sensitive homogeneous polymer blend comprising a hydrolytically degradable polymer and a water-soluble polymer formed into a homogeneous polymer blend.



# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 97/22794

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08L29/04 C08L67/04 //(C08L29/04, 67:04), (C08L67/04, 29:04)

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 567 510 A (PATNODE GREGG A ET AL) 22 October 1996 cited in the application see claims; example 37	1-14
P, X	US 5 658 977 A (YANG XIAOMING ET AL) 19 August 1997 see column 3, line 34 - column 5, line 24; claims	14
X	WO 94 10257 A (NAT STARCH CHEM INVEST) 11 May 1994 see claims	1-14
X	EP 0 654 504 A (TOYO SEIKAN KAISHA LTD) 24 May 1995 see claims; examples	14
	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

24 April 1998

Date of mailing of the international search report

07/05/1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

DE LOS ARCOS, E

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 97/22794

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>IKEJIMA T ET AL: "INFRARED ANALYSIS ON BLENDS OF POLY(3-HYDROXYBUTYRIC ACID) AND STEREOREGULAR POLY(VINYL ALCOHOL): INFLUENCE OF TACTICITY OF POLY(VINYL ALCOHOL) ON CRYSTALLIZATION OF POLY(3-HYDROXYBUTYRIC ACID)"</p> <p>MACROMOLECULAR CHEMISTRY AND PHYSICS, vol. 197, no. 3, 1 March 1996, pages 869-880, XP000598205</p> <p>see abstract</p>	14

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 97/22794

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5567510 A	22-10-96	US 5472518 A	05-12-95
		AU 4240496 A	24-07-96
		CA 2206921 A	11-07-96
		EP 0800595 A	15-10-97
		WO 9621057 A	11-07-96
		US 5630972 A	20-05-97
		US 5508101 A	16-04-96
US 5658977 A	19-08-97	NONE	
WO 9410257 A	11-05-94	US 5312850 A	17-05-94
		US 5252646 A	12-10-93
		AU 659353 B	11-05-95
		AU 5133293 A	24-05-94
		CA 2126849 A	11-05-94
		EP 0618948 A	12-10-94
		JP 7502069 T	02-03-95
EP 0654504 A	24-05-95	JP 2658837 B	30-09-97
		JP 7285528 A	31-10-95
		AU 679126 B	19-06-97
		AU 7889594 A	25-05-95